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(54) Title: COMPOSITE METAL PRODUCT AND METHOD FOR THE MANUFACTURING OF SUCH A PRODUCT

$$\frac{N}{C+N}$$

(I) (57) Abstract: The invention concerns a composite metal product, which contains 30-90 vol-% of a hard phase in the form of particles of substantially M(C,N)-carbonitride or M(C,N,O)-carbonitrideoxide, commonly referred to as hard phase of MX-type, where M to at least 50 atomic-% consists of titanium, which particles are essentially homogenously distributed in a matrix consisting of a hardenable steel, and wherein the atomic-% ratio between C and N shall satisfy the condition $0.1 < (\text{formula I}) < 0.7$. At the manufacturing of the product, a powder mixture, which contains powder of titanium carbide, titanium nitride, and/or titanium carbonitride in such an amount that its content of titanium atoms correspond to at least 50 % of the metal atoms in said hard phase of MX-type in the final metal product, and at least the main part of other constituents of the final metal product, is milled together. A green body is formed of the milled product, and the green body is subjected to liquid phase sintering at a temperature of 1350-1600 °C and subsequently cooled, causing the liquid phase to solidify, wherein, during said liquid phase sintering and subsequent cooling, said hard phase particles of MX-type obtain their final composition and size.

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COMPOSITE METAL PRODUCT AND METHOD FOR THE MANUFACTURING OF SUCH A PRODUCT

TECHNICAL FIELD

- 5 The present invention concerns a composite metal product suitable to be used as a material for shearing, cutting, punching and moulding tools as well as for wearing parts and construction elements, when high demands are raised on hardness and wear resistance in combination with an adequate strength. The invention also relates to a method for the manufacturing of such product.

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BACKGROUND OF THE INVENTION

- For materials for shearing, cutting, punching and moulding tools as well as for wearing parts and construction elements, on which high demands are raised on hardness and wear resistance, today cold work steels, high speed steels, cemented carbide materials, and ceramic materials are employed. In this series, high speed steels are generally considered to be more qualified than cold work steels, cemented carbide materials more qualified than high speed steels, and so on. While the dividing lines between cold work steels and high speed steels have more or less been erased, mainly due to the employment of powder technology, there is still a wide gap between high speed steels and highly qualified cemented carbide materials. The concept of "cemented carbide materials" means materials having an extremely high content of carbides which are sintered together in a binder metal, which normally consists of a cobalt base alloy. Many attempts have been made during the last fifty years to bridge this gap through the development of steel alloys having a high content of titanium carbides. An early suggested material belonging to this category is known under the trade name "Ferro-TiC", which however achieved only limited practical use. Another material having the trade name "Coronite", which is disclosed in the US Patent No 4,145,213, is no longer on the market place, as far as is known to the applicant.

- 25 30 The material according to said US Patent No 4,145,213 contains a very high content of titanium carbide in a matrix consisting of hardenable steel. According to the patent, the titanium carbides in turn contain a larger amount of nitrogen than carbon. Further, according to the patent, the material may be produced through liquid phase sintering of a cold pressed powder body, or through liquid phase sintering of a powder body under pressure – so called pressure sintering -, through isostatic hot pressurising, or through forging of a powder body with or without the presence of liquid phase. When sintering with the presence of liquid phase it is necessary, in order to avoid any undesired grain

growth of the hard phase products, to perform the sintering operation during a very short period of time at the sintering temperature. This is a limitation which is serious, because it makes it difficult or impossible to achieve a desirably even distribution of the hard phase particles in the matrix. This may be the reason why none of the said technologies, as far as is known to the applicant, became employed for the commercial production of the Coronite-material. Instead, the material was made through extrusion; an expensive technique, which made it impossible for the material to compete with neither high speed steels nor cemented carbide materials. Any other material which can claim that it bridges the "gap" between high speed steels and cemented carbide materials is not known.

DISCLOSURE OF THE INVENTION

It is the purpose of the invention to provide a new material which can compete with presently available materials for tooling, including shearing, cutting, punching and/or moulding operations, as well as for other products on which high demands are raised as far as hardness and wear resistance are concerned. Particularly, it is an objective to provide an alternative to cemented carbide materials, at least for certain applications, which, however, does not exclude that the material may be employed, at least for certain applications, where high speed steels, cold work steels or wear resistant construction steels are used today.

This objective can be achieved through the invention by means of a composite metal product which contains 30-90 vol-% of a hard phase in the form of particles of substantially $M(C,N)$ -carbonitride or $M(C,N,O)$ -carbonitrideoxide, commonly referred to as hard phase of MX-type, where M to at least 50 atomic-% consists of titanium and the atomic-% ratio between C and N shall satisfy the condition $0.1 < \frac{N}{C+N} < 0.7$, preferably satisfy the condition $0.2 < \frac{N}{C+N} < 0.6$, suitably satisfy the condition $0.3 < \frac{N}{C+N} < 0.6$, and most conveniently satisfy the condition $0.4 < \frac{N}{C+N} < 0.5$, which particles are essentially homogenously distributed in a matrix consisting of a hardenable steel.

During the development work which resulted in the present invention, initial experiments were also made with metals other than titanium in said hard phase of MX-type, such as V, Nb and Hf. These initial experiments did not lead to desired results, as the portion of said elements was too high. Later experiments, however, indicate that

good results can be achieved if the MX-phase contains a more moderate content of one or more of said metals, for example niobium. Also other MX-phase forming metals might be conceived, such as Ta and Zr. However, it is judged that M not to more than max. 40 atomic-%, preferably max. 30 atomic-%, in said hard phase of MX-type may consist of one or more of the metals which belong to the group consisting of V, Nb, Ta, Hf, and Zr. For example, M might consist of at least 5 and max. 30 atomic-% V and/or of at least 5 and max. 30 atomic-% Nb, however, totally max. 40 atomic-%, preferably max. 30 atomic-%. If Ta, Zr and/or Hf shall be included, the total amount of those metals should not amount to more than 3 atomic-% of the total metal content of the hard phase of MX-type.

According to an aspect of the invention, the metal M in said hard phase of MX-type consists of titanium to at least 70 atomic-%, preferably at least 80 atomic-%, and most conveniently to at least 90 atomic-%.

The total content of hard phase of MX-type amounts, according to an aspect of the invention, to 30-70 vol-%, preferably to 40-60 vol-%, of the metal product.

The said matrix consists of a hardenable steel, as has been mentioned above. In its hardened and tempered condition, the steel may also contain secondarily precipitated carbides, e.g. vanadium carbides, i.e. MC-carbides, which have a size too small to be observed in an optical microscope. Further, the steel may contain primary carbides which are typical for high speed steels, e.g. M_6C -carbides. Thus said matrix including secondarily precipitated MC-carbides, which may exist in the matrix, and any hard phase of other type than MX-type, which may exist in the matrix, may have the following chemical composition in weight-%:

0.3-3.0 C
from traces to max. 2 Si
from traces to max. 2 Mn
from traces to max. 0.5 S
2-13 Cr
from traces to max. 18 W
from traces to max. 12 Mo
from traces to max. 15 Co
from traces to max. 10 V
from traces to max. 2 Nb

balance Fe, however at least 50 weight-% Fe, and normally existing impurities from the manufacturing of the steel.

The invention also aims at providing a method for manufacturing, with good
5 reproducibility, a composite metal product which contains 30-90 vol-% of a hard phase having the form of particles, which consist mainly of M(C,N)-carbonitride or M(C,N,O)-carbonitrideoxide, commonly referred to as hard phase of MX-type, which particles are substantially homogenously distributed in a matrix of hardenable steel. According to the method of the invention, this is achieved therein that a powder
10 mixture, which contains powder of titanium carbide, titanium nitride, and/or titanium carbonitride in such an amount that its content of titanium atoms correspond to at least 50 % of the metal atoms in said hard phase of MX-type in the final metal product, and at least the main part of other constituents of the final metal product, is milled together, that a body is formed of the milled mixture, and that said body is liquid phase sintered at
15 a temperature between 1350 and 1600 °C and subsequently cooled, causing the liquid phase to solidify, said hard phase particles of MX-type obtaining their final composition and size during said liquid phase sintering and subsequent solidification. Preferably, at least 90 % of the number of particles, which can be observed in a viewed section of the material by means an optical microscope, have a size smaller than 1 µm.

20 Further, according to an aspect of the invention, the contents of carbon and nitrogen are controlled during the integrated process, which comprises selection and milling of powder, milling the powder mixture, forming press bodies of the milled powder, and liquid phase sintering, such that the amounts of carbon and nitrogen in atomic-% in said
25 hard phase in the finished product will satisfy that value of the ratio $\frac{N}{C+N}$ which has been mentioned in the foregoing.

According to another aspect of the invention, the milling of the powder mixture is performed with a power supply of at least 10 MJ (megajoule)/kg powder, preferably at
30 least 20 MJ/kg powder. A power supply of 25 MJ/kg powder has turned out to be suitable. The power supply therefore, according to an aspect of the invention, should be limited to max. 50 MJ/kg powder, suitably be limited to max. 40 MJ/kg powder, in order not to make the manufacturing unnecessarily expensive.

35 It is a typical feature of the method of manufacturing the composite metal product, that hard phase particles of MX-type will be evenly distributed in the said matrix. Evenly

distributed means that not more than 0.5 % of a section of the product should consist of regions having a length of at least 8 μm in the direction of the longest extension of the region, a width crosswise said direction of the longest extension, in any section of the region, of not more than 8 μm , and an area of at least 50 μm^2 , which regions are void of hard phase particles of MX-type, and that not more than 10 %, and preferably not more than 5 % of the section of the product, consists of regions having a length of at least 6 d in the direction of the longest extension of the region, a width crosswise said direction of the longest extension, in any section of the region, of at least 6 d , and an area of at least $9 \pi d^2$ where d is the mean value of the size of the hard phase particles of MX-type in the longest extension of the particles in the observed section, which regions are void of hard phase particles of MX-type.

The powder of titanium carbide, titaniumnitride and/ titaniumcarbonitride, which is employed in the powder mixture, may be oxidised. Performed experiments thus have shown that a highly oxidised powder may be used, and that there is no need to reduce such oxidised powder before use, which is a significant advantage from a cost point of view. Nor need any measures be made to prevent further oxygen take up during the continued process, which includes milling, forming press bodies and sintering. Oxygen existing in the powder mixture, plus additional oxygen which may be picked up during the process, combine with the titanium existing in said hard phase, where the oxygen partly replaces carbon and/or nitrogen in the crystal lattice of the hard phase, in which case the hard phase may be defined as $M(\text{C},\text{N},\text{O})$ -carbonitrideoxide. According to an aspect of the invention, the content of oxygen in this hard phase is 0.01-4 atomic-% of the total content of $\text{C}+\text{N}+\text{O}$ in the hard phase.

Further aspects and characteristic features of the invention will be apparent from the following description and discussion and from the patent claims.

BRIEF DESCRIPTION OF THE DRAWINGS

In the following description of performed experiments, reference will be made to the accompanying drawings, in which

Fig.1 – Fig.5 show microstructures of samples made of a powder mixture containing TiC and TiN, the resulting hard phase having varying ratios $\frac{N}{C+N}$,

Fig.6 – Fig.10 show the microstructures of a composite product, having a chemical composition according to the invention, after sintering at varying temperatures between 1350 and 1540 °C,

Fig.11 shows the microstructure of a material having the same chemical composition, manufactured through hot isostatic pressing (HIP-ing), and

Fig.12 shows the microstructure of a steel with an addition of NbC according to an aspect of the invention.

5

DESCRIPTION OF PERFORMED EXPERIMENTS

At the experiments, different mixtures of pulverulent hard phase, base metal powder, and carbon in the form of graphite powder were used. The hard phase powder consisted of vanadium carbide (VC), niobium carbide (NbC), hafnium carbide (HfC), hafnium-titanium carbide ((Hf,Ti)C), titanium nitride (TiN), and titanium carbide (TiC). More specifically, there was used as hard phase commercially available powders of said hard phases with a powder grain size in the order of 1 μm . These powders contained several thousands ppm oxygen. In other words, they were highly oxidised. The order of the oxygen content could be estimated to about 4000 ppm (0.4 %) but could be even higher and amount to the order of 1 weight-%. The base metal powder consisted of a commercially available high speed steel obtained from the applicant's own production. This high speed steel is known by its trade name ASP 2030[®], which has the chemical composition in weight-%: 1.28 C, 0.5 Si, 0.3 Mn, 4.2 Cr, 5.0 Mo, 3.1 V, 6.4 W, 8.5 Co, balance Fe and unavoidable impurities. This powder consisted of a gas atomised powder, which was sieved to a maximal grain size of 125 μm . It was an aim at the experiments to achieve a matrix of the finished composite product, which should have essentially the same composition as the matrix of the added steel powder of grade ASP 2030[®] after hardening. Therefore also carbon was added in different amounts to the powder mixtures in the form of graphite powder. Also a variant of ASP 2030[®] was tested, referred to as ASP 20XX.

The different powder mixtures were milled in a so called attritor mill, which is a type of ball mill having milling balls made of a ball bearing steel. In contrast to conventional ball mills, however, in which the energy is supplied to the milling balls through the rotation of the mill housing, in an attritor mill, the energy is supplied to the balls by means of a rotating propeller. This affords a very high velocity to the milling bodies and hence a capacity to transfer more energy to the product which is being milled. Therefore, in an attritor mill, the supply of energy/time is about fifteen times larger than in a more conventional ball mill. This is important, because it promotes the homogenisation of the material that is being milled. During the milling, the particles that are being milled are crushed, deformed and repeatedly put together again. Due to the deformation, which is an important part of this treatment, a great amount of

dislocation energy is supplied to the product that is milled, leading to a changed, higher state of energy of the milled material. The energy which was supplied to the milled powder in this mode amounted to about 25 MJ (Megajoule)/kg powder. No milling liquid was used during the milling. The milling was performed at atmospheric pressure.

- 5 Pick up of oxygen through oxidation could take place during the handling of the powder.

The thus milled powder mixtures were pressed to the form of green bodies without addition of any pressing aid.

10

The green bodies were consolidated through liquid phase sintering in a vacuum furnace, heated by graphite electric heaters. The sintering temperatures were varied from 1300 to 1540 °C with a holding time of 30 min. at the sintering temperature.

- 15 Prior to mechanical tests, the samples were hardened from 1180 °C, followed by tempering at 560 °C, 3x1h.

Series of experiments I; samples containing vanadium carbide (VC) and titanium nitride (TiN)

- 20 In this series of experiments, three different alloys were prepared; alloys 63, 64 and 65. Besides VC, TiN, the base metal ASP 2030[®], and carbon in the form of graphite powder, also a small fraction of pulverent chromium carbide, Cr₃C₂, was added. The ingredients of the powder mixtures are given in Table 1.

Table 1 Ingredients (gram) of the powder mixtures

Alloy No	63	64	65
	g	g	g
ASP 2030 [®]	1668	1668	1668
VC	490	530	570
TiN	295	257	220
Cr ₃ C ₂	36	36	36
Carbon (graphite)	12	12	12

25

The powder mixtures were milled for ten hours in an attritor mill with an energy supply of about 25 MJ/kg powder, were pressed to green bodies, and were sintered in the mode described above. The microstructure of samples sintered at 1300, 1350 and 1400 °C were studied. For comparison, also samples of the same powder mixtures which had

- been consolidated through hot isostatic pressing (HIP-ing) were studied. The studies showed that it was possible to achieve, with these powder mixtures, a high density and small hard phase grain sizes after sintering. However, it was also noted that the homogeneity of the alloys was not improved through the sintering in comparison with
 5 HIP-ed materials. Moreover, an abnormal growth of the hard phase particles occurred, particularly in some major regions, in all the three alloys 63, 64 and 65.

Series of experiments II; samples containing niobium carbide (NbC) and titanium carbide (TiC)

- 10 Three mixtures of powder of the base alloy ASP 2030[®], niobium carbide, titanium nitride and carbon (graphite), having the same physical character as according to the series of experiments I, were prepared. The compositions of the mixtures are given in Table 2.

15 **Table 2 Ingredients of the powder mixtures**

Alloy No	74	75	76
	g	g	g
ASP 2030 [®]	1248	1274	1302
NbC	544	430	310
TiN	198	286	378
Carbon (graphite)	10	10	10

- After milling according to the mode described in the foregoing, and manufacturing of green bodies, consolidated samples were prepared through HIP-ing as well as through
 20 liquid phase sintering at 1350 °C and at 1400 °C. The microstructure studies of the samples demonstrated that HIP-ing gave a comparatively homogeneous microstructure. The homogeneity after liquid phase sintering, however, was not good. This can probably be attributed to poor wetting between the hard phase and the liquid phase. This type of alloy, containing a high fraction of NbC, was therefor not considered to be
 25 suitable for liquid phase sintering.

Series of experiments III; samples containing HfC, (Hf,Ti)C and TiN

Powder mixtures with compositions according to Table III were prepared. Also these powders had the same physical character as in the series of experiments I and II.

Table 3 Ingredients (gram) of the powder mixtures

Alloy No	66	67	68
	g	g	g
ASP 2030®	1188	1188	1188
HfC	984	590	262
(Hf,Ti)C	-	525	971
TiN	328	197	79
Carbon (graphite)	15	15	15

Also these powder mixtures were milled in a way which was analogous with that of the series of experiments I and II prior to the manufacturing of green bodies, which were consolidated through HIP-ing and sintering at 1400 °C and 1540 °C, respectively. Microstructure studies, however, could not show any significant improvement of the homogeneity through sintering at 1400 °C or at 1540 °C.

10 Series of experiments IV; samples containing TiC and TiN

The ingredients of the powder mixtures in this series of experiments are given in Table 4. The nominal chemical compositions (aimed values) are given in Table 5. The typical character of the powder was equivalent with that of the foregoing series of experiments.

15 **Table 4 Ingredients of the powder mixtures**

Alloy No	83	69	84	70	71	72	73
	g	g	g	g	g	g	g
ASP 2030®	1364	1697	1360	1692	1687	1682	1677
TiC	583	652	468	517	387	259	125
TiN	46	135	166	276	411	545	684
Carbon (graphite)	7	23	7	23	22	21	20

The ingredients of the powder mixtures were selected such that only the contents of carbon and nitrogen were varied, while the other elements existed in essentially equal amounts in the mixtures. Thus the chemical composition of the powder mixtures contained in weight-%: 0.39 Si, 0.18 Mn, 2.66 Cr, 3.34 Mo, 4.18 W, 2.05 V, 5.60 Co and 25.3 Ti. According to information received from the manufacturers of the

ingredients, the oxygen content amounted to about 0.27 weight-%. Balance was iron, carbon, nitrogen and unavoidable impurities. The contents of carbon and nitrogen in the powder mixtures are given in Table 5.

5 **Table 5 The contents of carbon and nitrogen, weight-%, of the powder mixtures**

Alloy No	69	70	71	72	73	83	84
	%	%	%	%	%	%	%
C	6.8	5.2	4.1	3.1	2.0	6.8	5.7
	0	2	9	5	7	8	5
N	1.2	2.4	3.6	4.8	6.1	0.5	1.8
	0	7	7	7	2	2	5

The powder mixtures were milled in an attritor mill in the mode which has been described in the foregoing, e.g. for a period time of 10 hours, with an energy supply of 25 MJ/kg powder. Green bodies were made of the milled powder, and the green bodies were consolidated through HIP-ing and through liquid phase sintering, respectively. The liquid phase sintering was carried out at varying temperatures between 1300 and 1540 °C during a holding time of 30 minutes at the sintering temperature.

15 Studies of the microstructures of the sintered samples showed that the homogeneity of the microstructures varied with the chemical composition of the samples. Homogeneity in this context means the degree of even distribution of the hard phase particles in the matrix alloy. Fig.1 – Fig.5 shows the microstructures of samples of the alloys 69, 70, 71, 72 and 73 after liquid phase sintering at 1480 °C. It is evident that the alloys 70 and 71 had a comparatively homogeneous microstructure and fine hard phase particles with sizes well below 1 µm. Alloy 69 had a comparatively more coarse hard phase structure. Alloy 72 had an inferior homogeneity and a higher porosity, while alloy 73 had the poorest homogeneity and highest porosity. The differences can be attributed to any of the following factors: the chemical composition of the powder mixtures, chemical reactions between existing elements during the liquid phase sintering, and take up or loss of light elements during milling and sintering. For example carbon may have been taken up from heat elements of graphite at the sintering operation. Also oxygen can be taken up from the environment as well as nitrogen during the milling process. Further, during the liquid phase sintering, various elements are dissolved in the liquid phase to be incorporated in the MX-phase, so that M will consist not entirely of titanium but to some degree also of vanadium and other metals from the base alloy ASP 2030®. A

minor fraction of titanium is also likely to be dissolved in the melt, despite that the solubility of titanium is low. Without binding the invention to any specific theories, it may be assumed that the reaction kinetics is comparatively low, at least for some of the alloys, which is favourable, because it makes it possible to perform the liquid phase sintering at a high temperature for a long period of time, without causing the carbides to grow to any unacceptable degree. Carbon can be assumed to promote the wetting between the hard phase and the liquid phase, but also a certain amount of nitrogen appears to be necessary in the hard phase, on one hand for stabilising the hard phase and, on the other hand also to allow a take up of oxygen, which will replace some carbon and/or nitrogen in the crystal lattice of the hard phase. It is further assumed that also existing M_6C -carbides enter the liquid phase during the sintering operation and that they may form a network around the $M(C,N,O)$ -particles during the solidification, an effect which can be minimised, e.g. through selection of a suitable base alloy having a lower content of W and Mo.

In order to investigate the significance of the chemical composition of, in the first place, the hard phase particles, the chemical composition of the hard phase, and also the chemical composition of the matrix alloy, has been studied by means of various techniques. EDS-analysis (Energy Dispersive Spectroscopy) and Thermo-Calc calculation were employed. The Thermo-Calc calculated compositions of the hard phase and the matrix at the hardening temperature 1180 °C, of some selected alloys which had been sintered at 1480 °C, are given in Tables 6 and 7. The oxygen content has not been considered at the Thermo-Calc calculations. It is considered to be negligible in the matrix but may amount to about 4 atomic-% of the total content of C+N+O in the hard phase.

Table 6 Calculated chemical composition of the hard phase of liquid phase sintered samples, weight-%, and the ratio $\frac{N}{N+C}$ of the hard phase

Alloy No	Ti %	V %	Cr %	Fe %	Co %	Mo %	W %	C %	Si %	N %	$\frac{N}{N+C}$
69	45,7	3,30	0,33	0,43	trace s	0,76	0,75	39,3	trace s	9,41	0,19
70	45,6	3,25	0,27	0,99	trace s	0,27	0,28	33,4	trace s	15,9	0,32
71	46,5	3,01	0,08	0,93	trace s	0,05	0,05	27,3	trace s	22,1	0,45
72	46,2	2,61	0,03	1,48	trace s	0,01	0,01	18,7	trace s	30,9	0,62
73	46,7	2,17	0,01	1,53	trace s	trace s	trace s	14,0	trace s	35,6	0,72

5 **Table 7** Calculated chemical composition of the matrix of liquid phase sintered samples, atomic-%

Alloy No	Ti %	V %	Cr %	Fe %	Co %	Mo %	W %	C %	Si %	N %
69	trace s	0,14	4,24	80,7	8,76	1,86	0,92	1,79	1,29	trace s
70	trace s	0,15	4,27	79,7	9,06	1,65	0,84	2,65	1,33	trace s
71	trace s	0,37	4,47	80,2	9,03	1,90	1,03	1,30	1,33	trace s
72	trace s	0,65	4,56	80,0	9,08	1,98	1,07	1,02	1,31	trace s
73	trace s	1,06	4,59	79,7	8,94	2,24	1,22	0,61	1,29	trace s

10 Through studies of the microstructures which are shown in Figs. 1-5 and in consideration of the chemical compositions of the hard phase given in Table 6, the conclusion can be drawn that the hard phase ought to have balanced contents of carbon

and nitrogen, expressed as atomic-%, which also has been stated in the disclosure of the invention in the introductory part of the description, as well as in the patent claims.

Fig. 1 shows that alloy 69, through sintering at 1480 °C, obtained a very good
5 homogeneity, containing hard phase particles with a mean size of about 0.8 µm, and that just very few particles had a size exceeding 1 µm. However, the homogeneity is more and more impaired and the hard phase particles are smaller and smaller, the higher the nitrogen fraction of the hard phase is, which is illustrated by Figs. 4-5. In order to test if the homogeneity of the samples, in which the hard phase contains somewhat more
10 carbon than nitrogen, can be influenced by the sintering temperature, samples of alloy 71 were examined after liquid phase sintering at temperatures varying between 1350 and 1540 °C. Also a HIP-ed sample of the same alloy was studied. The resulting microstructures are shown in Figs. 6-11. The microstructure after sintering at 1480 °C has been shown in Fig. 3. Fig. 6 shows that the microstructure after sintering at 1350 °C
15 was almost as inhomogenous as after HIP-ing, Fig. 11, but that the microstructure achieved a good homogeneity with very evenly distributed hard phase particles, with particle sizes well below 1 µm, through sintering at a temperature exceeding 1480 °C, as is shown in Figs. 9 and 10.

20 According to what has been disclosed above, a good homogeneity is promoted according to the invention through a controlled ratio $\frac{N}{C+N}$. This is also apparent from

Table 6 and Table 8. The latter table shows that also an increased sintering temperature efficiently improves the homogeneity of the microstructure, if the value of the ratio

$\frac{N}{C+N}$ suggested by the invention is satisfied. Table 8 shows the total area of major

25 regions in terms of percent of a studied area of a section of the material, which major regions are void of any visible particles of said MX-phase and have a length of at least 6 d in the direction of the longest extension of the regions, a width, in any section of the region, of at least 6 d in a direction crosswise said longest extension, and an area of at least $9 \pi d^2$, where d is the mean value of the sizes of hard phase particles of MC-type in
30 the longest extension of the particles in the viewed area of the section. The existence of such major, "empty" regions, can only partly be attributed to an insufficient milling prior to sintering, although the milling of the alloy metal, which consisted of the high speed steel ASP 2030® in the examples, is considered to be of significant importance. If the milling is insufficient, there may be as risk that the homogeneity derived through the
35 sintering operation will be insufficient, even if the condition concerning the value of the

ratio $\frac{N}{C+N}$ is satisfied and the sintering temperature is raised to the highest level

which in practice is possible. Also the results obtained for HIP-ed materials are included in table 8.

5 **Table 8 Area of major regions void of visible MX-phase particles in terms of % of total studied area**

Alloy No.	69	70	71	72	73
HIP/Sintering Temp. °C	%	%	%	%	%
HIP	39	33	38	42	42
1350	30		33	33	
1380	28	20		32	
1400	7		16		
1430	<5	10	25		
1480	<5	<5	20	23	32
1510		<5		17	21
1540		<5		13	11

The samples which were produced in the series of experiments IV were also subjected to mechanical tests. After hardening through dissolution treatment at 1180 °C, cooling
 10 to room temperature, and tempering three times at 560 °C, each time for 1 hour, the hardness at Vicker hardness tests amounted to between about 1080 and 1180 HV30, when the samples had a nominal composition. Take up of carbon and nitrogen increased the hardness up to between 1250 and 1300 HV30 for some alloys.

15 Series of experiments V; samples containing TiC, TiN and NbC

In this series, results will be reported from experiments with two different alloys, denominated alloy no 110 and alloy no 160, respectively. Besides TiC, TiN and NbC, the powder mixtures contained the base metal alloy ASP 2030® and a variant thereof, respectively, and carbon in the form of graphite powder. The variant had a lower
 20 content of Mo and W than ASP 2030®, and is referred to as ASP 20XX in the following. The powder mixture of alloy 110 also contained a minor amount of vanadium carbide, VC. The powders had the same physical character as the powders in the foregoing series of experiments. The ingredients are given in Table 9.

Table 9 Ingredients (gram) of the powder mixtures

Alloy No	110	160
	g	g
ASP 2030 [®]	1343	
ASP 20XX		1273
TiC	343	373
TiN	219	213
VC	34	
NbC	46	137
Carbon (graphite)	5	4

- 5 The powder mixtures were milled in the same mode as in the series of experiments IV. Green bodies were prepared of the milled powders, and the green bodies were liquid phase sintered at temperatures varying between 1400 and 1540 °C during a holding time of 30 minutes at the sintering temperature.
- 10 Besides Ti(C,N) and a matrix, alloy 110 also contained M₆C- carbides, in which M substantially consisted of molybdenum and tungsten, and MC- carbides, which substantially consisted of vanadium carbides. In spite of the presence of vanadium carbides, the V-content of the hard phase was about 50 % less than what could be expected in view of the total composition of the alloy. The contents of niobium and
- 15 vanadium in the hard phase of alloy 110 amounted to about 4 atomic-% and about 5 atomic-%, respectively, of the total content of M in the hard phase. In alloy 160, the content of niobium in the hard phase amounted to about 15 atomic-% of the content of metal M. The chemical contents of C and N in the hard phases amounted to about 4.6 weight-% C and 3.6 weight-% nitrogen in alloy 110, and to about 5.1 weight-% C and
- 20 3.6 weight-% N in alloy 160, respectively. The ratio $\frac{N}{C+N}$ for the hard phase of alloy no 110 thus was $3.6/(3.6+4.6)=0.43$, and the same value was obtained for alloy no 160: $3.9/(3.9+5.1)=0.43$.

- 25 A tool member was manufactured of alloy no 110 in the form of a cutter bit, intended to be used as an insert in a single tooth cutter. Prior to assembling, the insert was hardened from 1100 °C, followed by tempering at 560 °C/3x1h. The cutting capacity of the insert

was compared with that of an equal insert, made of the highly qualified, powder metallurgy manufactured high speed steel ASP 2030®. A relative productivity in terms of cutting capacity was achieved by means of the insert made of the alloy according to the invention, which was about two times larger (80-100 % larger) than that of the
5 known high speed steel. In this connection, it should also be mentioned that the material of the invention was manufactured at an experimental scale, i.e. with a technique which has great restrictions as far the cleanliness and other features of the produced material are concerned. Thus, further improvements should be possible to achieve at a full scale production. If the tool member – the insert – on the other hand was made of a sintered
10 carbide material, one should also have reason to count on an additional increase of the cutting capacity, which confirms that the composite metal product of the invention may fill the gap between high speed steels and sintered carbide materials.

Alloy no 160 was studied with reference to the microstructure after a heat treatment,
15 which comprised hardening from 1150 °C, but which in other respects was performed in the same way as for alloy no 110 according to the above; see Fig. 12, which shows a homogenous microstructure of essentially evenly distributed, rounded carbides in the hardened and tempered matrix.

20 The toughness was not quantified in terms of absolute magnitudes at toughness measurements. In comparison with samples which had been manufactured through HIP-ing, however, no systematic difference could be notified between HIP-ed samples and samples which had been subjected to liquid phase sintering according to the invention.

25 DISCUSSION

As may be concluded from the foregoing description of performed experiments, very good results were achieved in the series of experiments IV. In that series, there were used, as starting materials, powder mixtures containing titanium carbide and titanium nitride, and in other respects the process was controlled such that the contents of carbon
30 and nitrogen could satisfy the balanced relations which have been indicated in the foregoing. Also the importance of the milling and of the sintering temperature for the achievement of the desired microstructure has been discussed. On the other hand, the importance of the composition of the matrix alloy has not been investigated in any detail. As a base alloy in the powder mixtures, in the first place a high speed steel of
35 type ASP 2030® was used. This steel alloy provides, in the finished product, a matrix which can be hardened to a hardness ≥ 500 HV30. However, it is not sure that the chemical composition of that high speed steel is the most suitable one, in order, in

- combination with the other constituents of the powder mixture, to provide a matrix having an optimal chemical composition. For example, ASP 2030[®] has a comparatively high content of metals, which may form M_6C -carbides. It is true that carbides of that type can be dissolved during the liquid phase sintering according to the invention, but it is also true that they can be re-established in the matrix and/or on the $M(C,N)$ - and/or on the $M(C,N,O)$ - phase particles, which may be disadvantageous. Instead of ASP 2030[®], therefor a high speed steel having a lower content of W and Mo may be more suitable, as has been demonstrated in the foregoing with reference to the use of the alloy ASP 20XX in the series of experiments V. Also other steel alloys are conceivable, high speed steels as well as other hardenable steels, e.g. cold work steels. However, as a base alloy there should preferably be used a steel alloy, which in combination with other constituents provides a matrix in the finished material, which matrix can be hardened to a hardness ≥ 500 HV30 after tempering.
- Also the content of hard phase in the powder mixture can be varied. Besides titanium carbide-, titanium nitride-, and/or titanium carbonitride powders, one may thus, at least for certain applications, consider moderate additions of other carbides or nitrides of MX-type, such as VC, NbC, TaC, ZrC, HfC, and/or (HfTi)C and corresponding nitrides, however not more than 30 mol-% of the total content of the achieved hard phase of MX-type in the finished product. An advantage of e.g. stimulating the generation of mixed carbonitrides, in which a significant content of vanadium and/or niobium is present, may be that the formation of a dense material is accelerated even when sintering at a relatively low temperature, which could justify the addition of a certain amount of VC and/or NbC in the powder mixture or a higher content of vanadium and/or niobium in the base metal alloy. For example niobium carbide in the powder mixture also might stimulate the milling. One might also conceive that mixed carbonitrides will be harder than pure titanium carbonitrides or pure titanium carbonitrideoxides, which could increase the hardness of the manufactured metal product. The results obtained in the series of experiments V indicate that especially the presence of a small or moderate content of NbC in the powder mixture, with or without a concurrent presence of VC, may provide a final product which has a desired combination of features. It is therefor estimated to be beneficial that 3-40 atomic-% of the metal atoms of the hard phase consist of (Nb+V), preferably at least 5 and max. 30 atomic-% Nb and/or V.

PATENT CLAIMS

1. A composite metal product, characterized in that it contains 30-90 vol-% of a hard phase in the form of particles of substantially M(C,N)-carbonitride or M(C,N,O)-carbonitrideoxide, commonly referred to as hard phase of MX-type,
5 where M to at least 50 atomic-% consists of titanium, which particles are essentially homogenously distributed in a matrix consisting of a hardenable steel, and that the atomic-% ratio between C and N shall satisfy the condition $0.1 < \frac{N}{C+N} < 0.7$.
2. A product according to claim 1, characterized in that the atomic-% ratio
10 between C and N shall satisfy the condition $0.2 < \frac{N}{C+N} < 0.6$.
3. A product according to claim 2, characterized in that the atomic-% ratio between C and N shall satisfy the condition $0.3 < \frac{N}{C+N} < 0.6$.
- 15 4. A product according to claim 3, characterized in that the atomic-% ratio between C and N shall satisfy the condition $0.4 < \frac{N}{C+N} < 0.5$.
5. A product according to any of claims 1-4, characterized in that 90 % of the number of said hard phase particles has a size, the longest extension of which is
20 smaller than 1 μm in a view section of the product.
6. A product according to any of claims 1-5, characterized in that not more than 10 % of a section of the product consists of regions having a length of at least 6 d in the direction of the longest extension of the region, a width crosswise said
25 direction of longest extension, in any section of the region, of at least 6 d , and an area of at least $9 \pi d^2$ where d is the mean value of the size of the hard phase particles of MX-type in the longest extension of the particles in the observed section, which regions are void of hard phase particles of MX-type.
- 30 7. A product according to any of claims 1-6, characterized in that not more than 0.5 % of a section of the product consists of regions having a length of at least 8 μm in the direction of the longest extension of the region, a width crosswise said direction of longest extension, in any section of the region, of not more than 8 μm ,

and an area of at least $50 \mu\text{m}^2$, which regions are void of hard phase particles of MX-type.

- 5 8. A product according to claim 1, characterized in that M in said hard phase to at least 70 atomic-% consists of titanium.
9. A product according to claim 8, characterized in that M in said hard phase to at least 80 atomic-% consists of titanium.
- 10 10. A product according to claim 9, characterized in that M in said hard phase to at least 90 atomic-% consists of titanium.
11. A product according to any of claims 1-10, characterized in that max. 40 atomic-% of M in said hard phase of MX-type consists of (V+Nb).
- 15 12. A product according to claim 11, characterized in that max. 30 atomic-% of M in said hard phase consists of or more of the metals which belong to the group consisting of V, Nb, Ta, Hf and Zr.
- 20 13. A product according to claim 11 or 12, characterized in that max. 25 atomic-% of M in said hard phase consists of Nb.
14. A product according to claim 13, characterized in that max. 15 atomic-% of M in said hard phase consists of Nb.
- 25 15. A product according to any of claims 1-14, characterized in that at least 2 atomic-% of M in said hard phase consists of V.
16. A product according to claim 15, characterized in that at least 5 atomic-% of M in said hard phase consists of V.
- 30 17. A product according to claim 15 or 16, characterized in that max. 15 atomic-% of M in said hard phase consists of V.
18. A product according to any of claims 1-17, characterized in that at least 2 atomic-% of M in said hard phase consists of Nb.

19. A product according to claim 18, characterized in that at least 5 atomic-% of M in said hard phase consist of Nb.
20. A product according to any of claims 1-19, characterized in that max. 3 atomic-% of M in said hard phase consists of Ta, max. 3 atomic-% of Zr, and max. 3 atomic-% of Hf.
21. A product according to claim 20, characterized in that said hard phase of MX-type does not contain Ta, Zr or Hf at levels exceeding impurity levels.
22. A product according to any of claims 1-21, characterized in that it contains 30-70 vol-% of said hard phase of MX-type.
23. A product according to claim 22, characterized in that it contains 40-60 vol-% of said hard phase of MX-type.
24. A product according to any of claims 1-23, characterized in that said hard phase of MX-type contains oxygen in an amount of 0.01-4 atomic-% of the total content of C+N+O in said hard phase.
25. A product according to any of claims 1-24, characterized in that said matrix including secondarily precipitated MC-carbides, which may exist in the matrix, and any hard phase of other type than MX-type, which may exist in the matrix, has the following chemical composition in weight-%:
- 0.3-3.0 C
from traces to max. 2 Si
from traces to max. 2 Mn
from traces to max. 0.5 S
2-13 Cr
from traces to max. 18 W
from traces to max. 12 Mo
from traces to max. 15 Co
from traces to max. 10 V
from traces to max. 2 Nb
balance Fe, however at least 50 weight-% Fe, and normally existing impurities from the manufacturing of the steel.

26. A product according to claim 25, characterized in that the matrix contains max. 2 weight-% Nb.
27. A product according to claim 25 or 26, characterized in that said matrix,
5 including any secondarily precipitated MC-carbides and any hard phase of other type than MX-type, which may exist in the matrix, has a chemical composition which contains max. 1 weight-% Si and 3-10 weight-% Cr.
28. A product according to claim 27, characterized in that the content of
10 (W+Mo+V) in said matrix, including any secondarily precipitated MC-carbides and any hard phase of other type than MX-type, which may exist in the matrix, amounts to at least 10 weight-%.
29. A product according to claim 27, characterized in that the content of
15 (W+Mo+V) in said matrix, including any secondarily precipitated MC-carbides and any hard phase of other type than MX-type, which may exist in the matrix, amounts to max. 10 weight-%.
30. A product according to claim 28, characterized in that said matrix,
20 including any secondarily precipitated MC-carbides and any hard phase of other type than MX-type, which may exist in the matrix, has a chemical composition, which contains, in weight-%, 3-7 Cr and 10-20 (W+Mo+V).
31. A product according to claim 29, characterized in that said matrix,
25 including any secondarily precipitated MC-carbides and any hard phase of other type than MX-type, which may exist in the matrix, has a chemical composition, which contains, in weight-%, 2-7Cr and 5-10 (W+Mo+V).
32. A method for manufacturing a composite metal product which contains 30-90 vol-%
30 of a hard phase having the form of particles, which consist mainly of M(C,N)-carbonitride or M(C,N,O)-carbonitrideoxide, commonly referred to as hard phase of MX-type, which particles are substantially homogeneously distributed in a matrix of hardenable steel, characterized in that a powder mixture, which contains
35 powder of titanium carbide, titanium nitride, and/or titanium carbonitride in such amount that its content of titanium atoms correspond to at least 50 % of the metal atoms in said hard phase of MX-type in the final metal product, and at least the main part of other constituents of the final metal product, is milled together, that a body is

formed of the milled mixture, and that said body is liquid phase sintered at a temperature between 1350 and 1600 °C and subsequently cooled, causing the liquid phase to solidify, said hard phase particles of MX-type obtaining their final composition and size during said liquid phase sintering and subsequent solidification.

- 5
33. A method according to claim 32, characterized in that the contents of carbon and nitrogen are controlled during the integrated process, which comprises selection and mixing of powders, milling the powder mixture, forming a green body of the milled powder mixture, and liquid phase sintering the green body, such that the contents of carbon and nitrogen of said hard phase of the final product, expressed in atomic-%, satisfy the ratio $0.1 < \frac{N}{C+N} < 0.7$.
- 10
34. A method according to claim 33, characterized in that the contents of carbon and nitrogen are controlled during the integrated process, which comprises selection and mixing of powders, milling the powder mixture, forming a green body of the milled powder mixture, and liquid phase sintering the green body, such that the contents of carbon and nitrogen of said hard phase of the final product, expressed in atomic-%, satisfy the ratio $0.2 < \frac{N}{C+N} < 0.6$.
- 15
35. A method according to claim 34, characterized in that the contents of carbon and nitrogen are controlled during the integrated process, which comprises selection and mixing of powders, milling the powder mixture, forming a green body of the milled powder mixture, and liquid phase sintering the green body, such that the contents of carbon and nitrogen of said hard phase of the final product, expressed in atomic-%, satisfy the ratio $0.3 < \frac{N}{C+N} < 0.6$.
- 20
36. A method according to claim 35, characterized in that the contents of carbon and nitrogen are controlled during the integrated process, which comprises selection and mixing of powders, milling the powder mixture, forming a green body of the milled powder mixture, and liquid phase sintering the green body, such that the contents of carbon and nitrogen of said hard phase of the final product, expressed in atomic-%, satisfy the ratio $0.4 < \frac{N}{C+N} < 0.5$.
- 25
- 30

37. A method according to any of claims 32-36, characterized in that the milling of the powder mixture is carried out with a supply of energy of at least 10 MJ (megajoule)/kg powder.

5 38. A method according to claim 37, characterized in that the milling of the powder mixture is carried out with a supply of energy of at least 20 MJ /kg powder.

39. A method according to claim 37 or 38, characterized in that the milling of the powder mixture is carried out with a supply of energy 10-50 MJ /kg powder.

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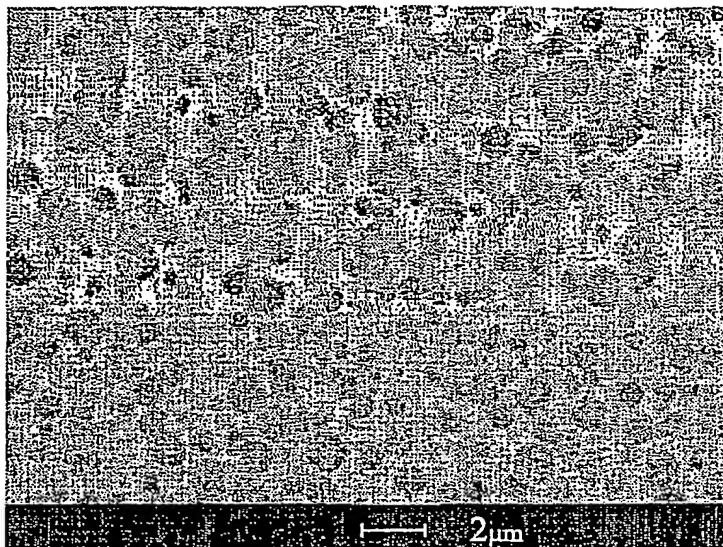
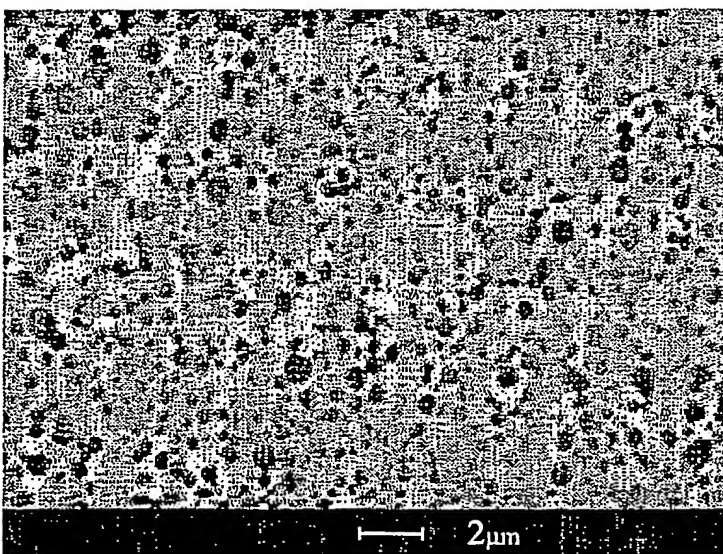
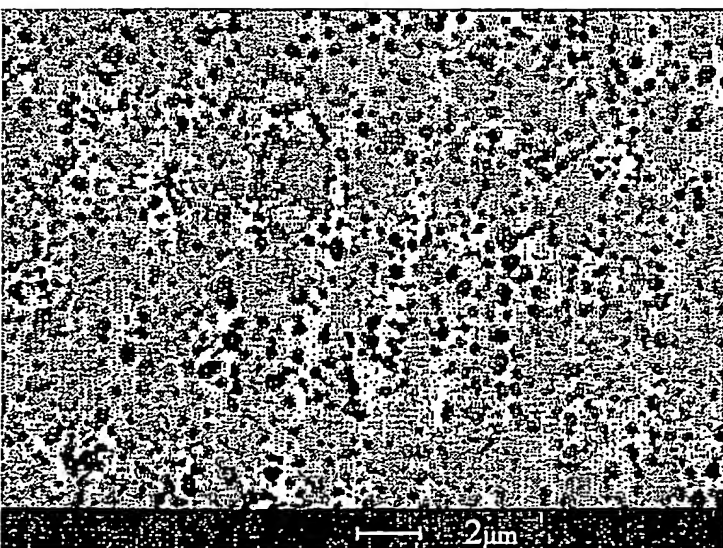
40. A method according to any of claims 32-39, characterized in that the content of oxygen is controlled during said integrated process such that the content of oxygen in the final product amounts to 0.01-4 atomic-% counted on the total content of C+N+O in the hard phase.

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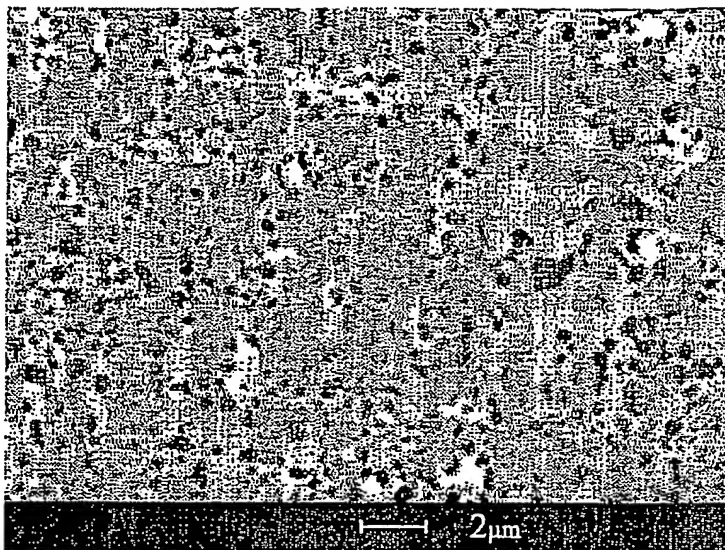
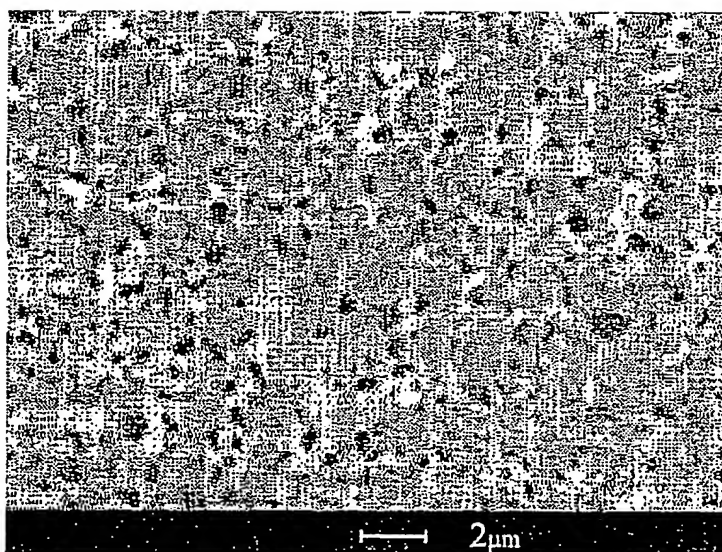
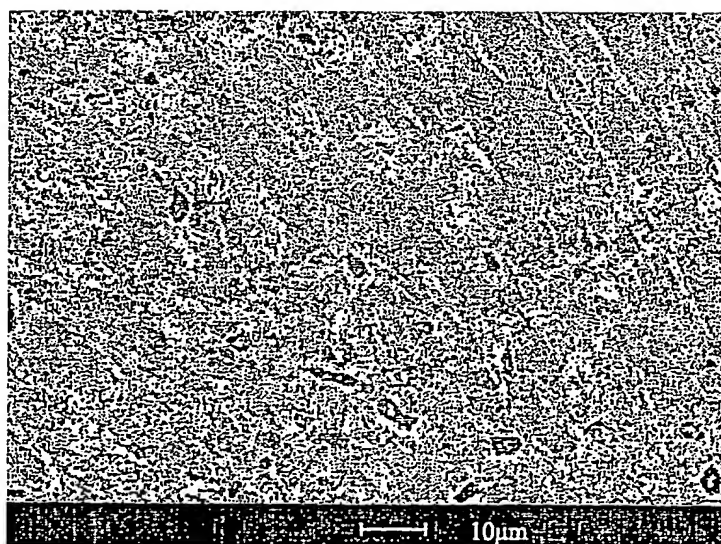
41. A method according to any of claims 32-40, characterized in that the liquid phase sintering is carried out at a temperature of 1450-1510 °C during a holding time of between 10 minutes and 2 hours at the sintering temperature, preferably during a holding time of 10-60 minutes.

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**Fig. 1****Fig. 2****Fig. 3**

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**Fig. 4****Fig. 5****Fig. 6**

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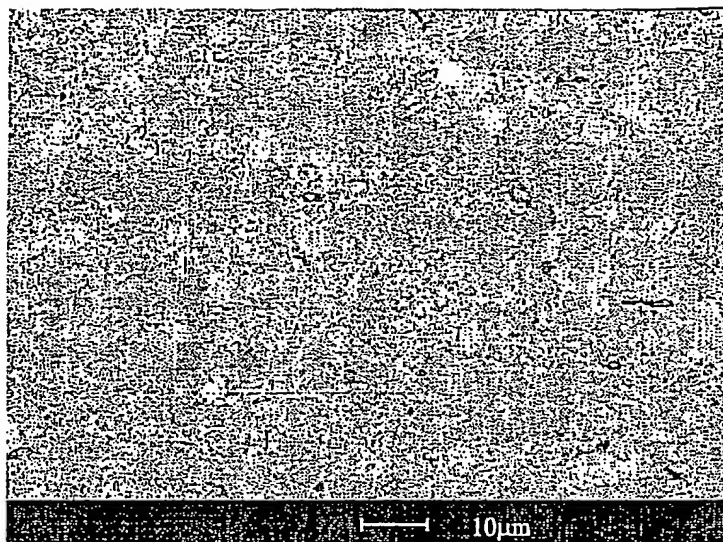


Fig. 7

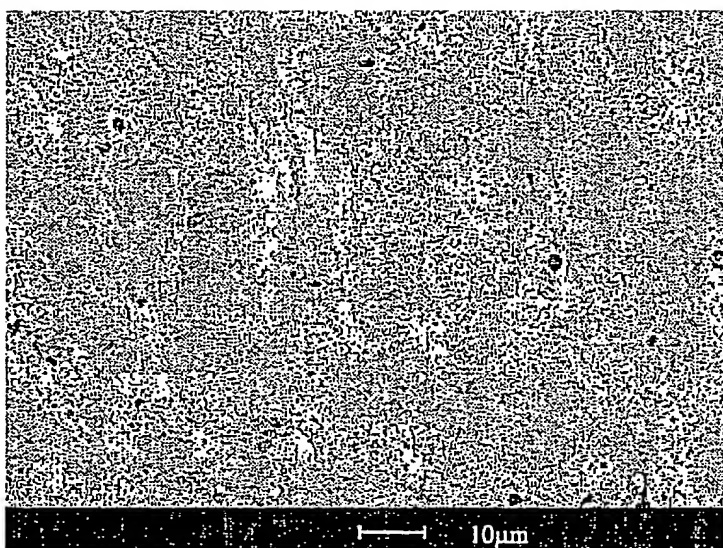


Fig. 8

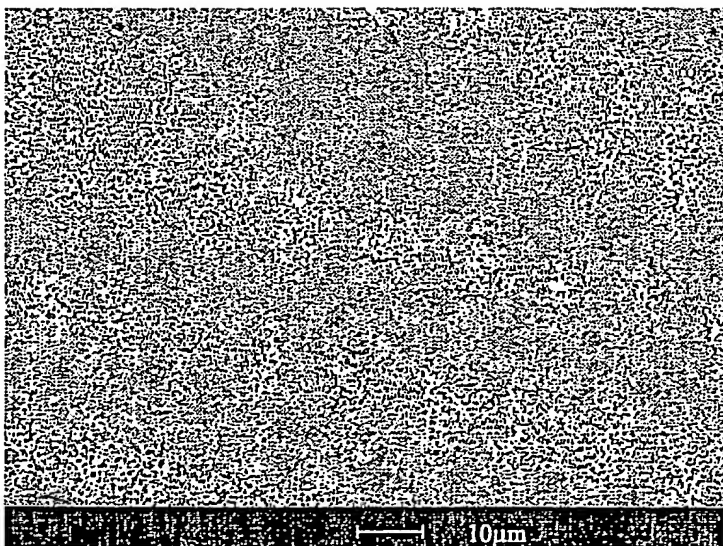
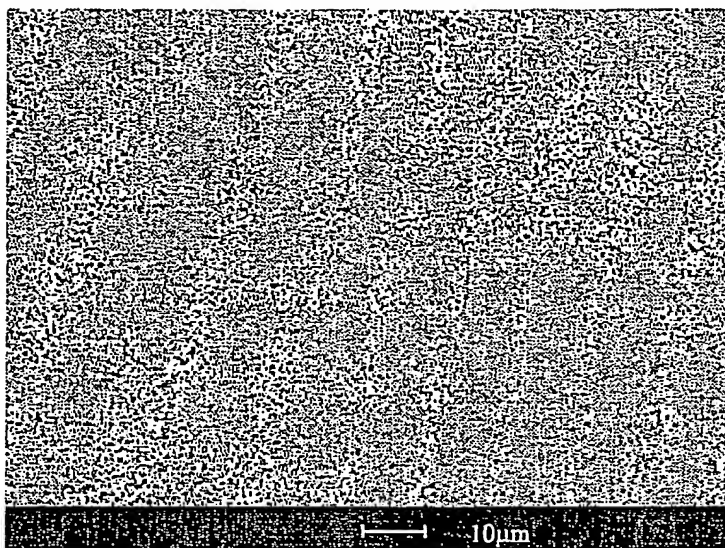
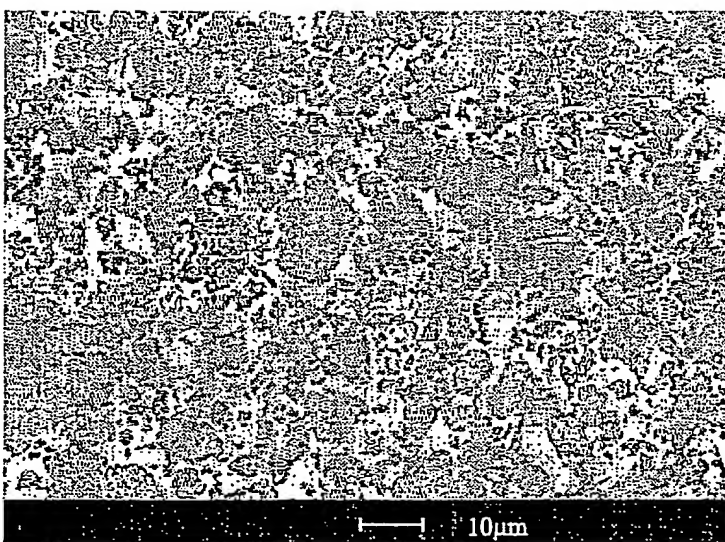
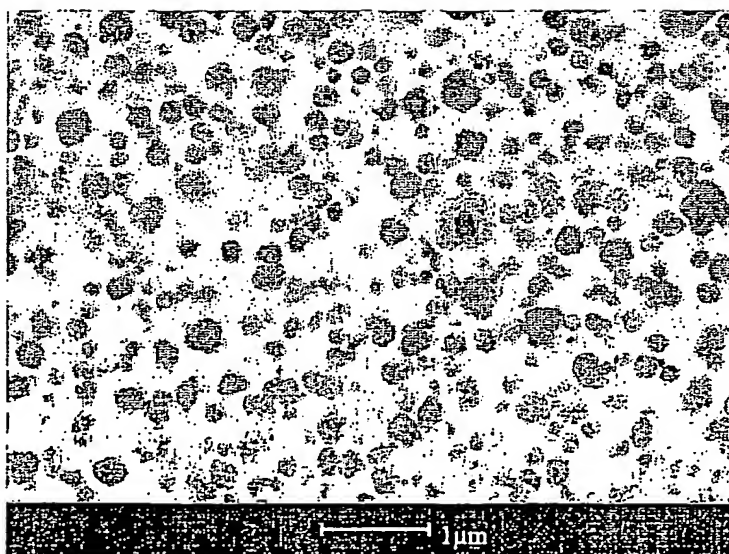


Fig. 9

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**Fig. 10****Fig. 11****Fig. 12**

INTERNATIONAL SEARCH REPORT

International application No.

PCT 2003/001908

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C22C 29/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4145213 A (ROLF G. OSKARSSON ET AL), 20 March 1979 (20.03.1979), column 2, line 48 - line 63, abstract --	1-33
A	US 6124040 A (HANS KOLASKA ET AL), 26 Sept 2000 (26.09.2000), column 2, line 32 - line 36, abstract --	1-33
A	DATABASE WPI Week 198436 Derwent Publications Ltd., London, GB; Class M21, AN 1984-223142 & JP 59133352 A (FUJI DICE KK et al) 31 July 1984 (1984-07-31) abstract --	1-33

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search

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Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 2003/001908

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Week 199536 Derwent Publications Ltd., London, GB; Class L02, AN 1995-273162 & JP 7173568 A (HITACHI TOOL KK) abstract</p> <p style="text-align: center;">-- -----</p>	1-33

INTERNATIONAL SEARCH REPORT

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